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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
31 December 2003 (31.12.2003)

PCT

(10) International Publication Number  
**WO 2004/001188 A1**

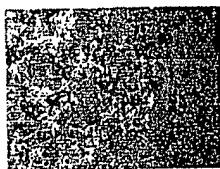
- (51) International Patent Classification<sup>7</sup>: E21B 43/26,  
43/25
- (21) International Application Number:  
PCT/EP2003/006188
- (22) International Filing Date: 12 June 2003 (12.06.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
10/177,815 20 June 2002 (20.06.2002) US
- (71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; 525-3rd Avenue S.W., Calgary, Alberta T2P 0G4 (CA).
- (71) Applicant (for FR only): SERVICES PETROLIERS SCHLUMBERGER [FR/FR]; 42 rue Saint Dominique, 75007, F-75007 Paris (FR).
- (71) Applicant (for GB, JP, NL only): SCHLUMBERGER HOLDINGS LIMITED [——]; PO Box 71, Craigmuir Chambers, Road Town, Tortola (VG).
- (71) Applicant (for AM, AT, AZ, BY, DE, DK, HR, IT, KG, KR, KZ, MD, NO, NZ, PL, RO, RU, TJ, TM, UA, ZA only): SCHLUMBERGER TECHNOLOGY B.V. [NL/NL]; Parkstraat 83-89, NL-2514 JG The Hague (NL).
- (71) Applicant (for AE, AG, AL, AU, BA, BB, BE, BF, BG, BJ, BR, BZ, CF, CG, CH, CI, CM, CN, CO, CR, CU, CY, CZ, DM, DZ, EC, EE, ES, FI, GA, GD, GE, GH, GM, GN, GQ, GR, GW, HU, ID, IE, IL, IN, IS, KE, KP, LC, LK, LR, LS, LT, LU, LV, MA, MC, MG, MK, ML, MN, MR, MW, MX, MZ, NE, NI, OM, PH, PT, SC, SD, SE, SG, SI, SK, SL, SN, SZ, TD, TG, TN, TR, TT, TZ, UG, UZ, VC, VN, YU, ZM, ZW only): SOFITECH N.V. [BE/BE]; Rue de Stalle 140, B-1180 Brussels (BE).
- (72) Inventors: LEE, Jesse; 5519 Chesapeake Place, Sugar Land, TX 77479 (US). NELSON, Erik; 10610 Willowisp Drive, Houston, TX 77035 (US).
- (74) Agent: MENES, Catherine; Etudes et Productions Schlumberger, 1, Rue Becquerel, BP 202, 92140 Clamart, F-92140 Clamart (FR).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR TREATING SUBTERRANEAN FORMATION



A



D



E



F

WO 2004/001188 A1

(57) Abstract: It has been found that a large variety of solid chemicals available in a bulk powder form could be added to subterranean treatment fluids with delayed release when said chemicals are delivered as capsules consisting of encapsulated granulates obtained by aggregating the bulk powder under pressure to form a densified material and optionally, dry comminuting said densified material to produce granulates at the desired size. The invention is particularly useful for delivering new types of breaking agents for stimulation fluids or additives for wellbore cementing.

## METHOD FOR TREATING SUBTERRANEAN FORMATION

### FIELD OF THE INVENTION

[0001] The present invention relates to the art of treating subterranean formations and more particularly, to a method of delivering material into a formation with a controlled delayed release. The invention is in particular applicable to the preparation of encapsulated breaking agents.

### BACKGROUND OF THE INVENTION

[0002] Hydraulic fracturing of subterranean formations has long been established as an effective means to stimulate the production of hydrocarbon fluids from a wellbore. In hydraulic fracturing, a well stimulation fluid (generally referred to as a fracturing fluid) is injected into and through a wellbore and against the surface of a subterranean formation penetrated by the wellbore at a pressure at least sufficient to create a fracture in the formation. Usually a "pad fluid" is injected first to create the fracture and then a fracturing fluid, often bearing granular propping agents, is injected at a pressure and rate sufficient to extend the fracture from the wellbore deeper into the formation. If a proppant is employed, the goal is generally to create a proppant filled zone from the tip of the fracture back to the wellbore. In any event, the hydraulically induced fracture is more permeable than the formation and it acts as a pathway or conduit for the hydrocarbon fluids in the formation to flow to the wellbore and then to the surface where they are collected.

[0003] The fluids used as fracturing fluids have also been varied, but many if not most are aqueous based fluids that have been "viscosified" or thickened by the addition of a natural or synthetic polymer (crosslinked or uncrosslinked) or a viscoelastic surfactant. The carrier fluid is usually water or a brine (e.g., dilute aqueous solutions of sodium chloride and/or potassium chloride).

[0004] The viscosifying polymer is typically a solvatable (or hydratable) polysaccharide, such as a galactomannan gum, a glycomannan gum, or a cellulose derivative. Examples of such polymers include guar, hydroxypropyl guar, carboxymethyl guar, carboxymethylhydroxyethyl guar, hydroxyethyl cellulose, carboxymethyl-hydroxyethyl cellulose, hydroxypropyl cellulose, xanthan,

polyacrylamides and other synthetic polymers. Of these, guar, hydroxypropyl guar and carboxymethylhydroxyethyl guar are typically preferred because of commercial availability and cost performance.

[0005] In many instances, if not most, the viscosifying polymer is crosslinked with a suitable crosslinking agent. The crosslinked polymer has an even higher viscosity and is even more effective at carrying proppant into the fractured formation. The borate ion has been used extensively as a crosslinking agent, typically in high pH fluids, for guar, guar derivatives and other galactomannans. Other crosslinking agents include, for example, titanium crosslinkers, chromium, iron, aluminum, and zirconium.

[0006] Viscoelastic surfactant fluids are normally made by mixing into the carrier fluid appropriate amounts of suitable surfactants such as anionic, cationic, nonionic and zwitterionic surfactants. The viscosity of viscoelastic surfactant fluids is attributed to the three dimensional structure formed by the components in the fluids when the concentration of viscoelastic surfactants significantly exceeds a critical concentration, surfactant molecules aggregate into micelles, which can become highly entangled to form a network exhibiting elastic behavior.

[0007] Viscoelastic surfactant solutions are usually formed by the addition of certain reagents to concentrated solutions of surfactants, frequently consisting of long-chain quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB). Common reagents that generate viscoelasticity in the surfactant solutions are salts such as ammonium chloride, potassium chloride, sodium salicylate and sodium isocyanate and non-ionic organic molecules such as chloroform. The electrolyte content of surfactant solutions is also an important control on their viscoelastic behaviour.

[0008] A key aspect of well treatment such as hydraulic fracturing is the "cleanup", e.g., removing from the fracture the carrier fluid (i.e., the base fluid without the proppant) after the treatment has been completed. Techniques for promoting fracture cleanup often involved reducing the viscosity of the fracture fluid as much as practical so that it will more readily flow back toward the wellbore.

[0009] Gel breakers are of common use for conventional polymer based fluids used in stimulation and the like since, unlike viscoelastic surfactant based fluid, conventional polymer-based fluids do not spontaneously break when contacted by hydrocarbons or

aqueous formation fluids and leaving a high viscosity fluid in the formation would result in a reduction of the formation permeability and consequently, a decrease of the production. The most widely used breakers are oxidizers and enzymes. The breakers can be dissolved or suspended in the liquid (aqueous, non-aqueous or emulsion) phase of the treating fluid and exposed to the polymer throughout the treatment (added "internally"), or exposed to the fluid at some time after the treatment (added "externally").

[0010] The most common external methods and compositions involve encapsulated enzymes or encapsulated oxidizers or involve the use of pre- or post-flushes that contain breakers. Breaking can occur in the wellbore, gravel pack, filter cake, the rock matrix, in a fracture, or in another added or created environment. See, for example, USP 4,741,401 (Walles et al.), assigned to Schlumberger Dowell and incorporated herein by reference.

[0011] Though viscoelastic-based fracturing fluids are spontaneously broken by hydrocarbon fluids contained in the formation fluids, it is sometimes suitable to better control the breaking. In U.S. Patent application 09/826,127, published January 10, 2002 under number 20020004464 incorporated herein by reference, several type of breakers are proposed including encapsulated salts such as ammonium persulfate, sodium salicylate, inorganic salts such as  $\text{NaPF}_6$  (sodium hexafluorophosphate) and KCl (potassium chloride).

[0012] Several mechanisms are typically involved in the release of an encapsulated material. Those mechanisms typically involve partial dissolution of the capsule enclosures, osmotic or chemical diffusion. However, since it is suitable that the breaking occurs no later than at the end of the fracturing operation, when the fracture closes due to formation pressure, a key mechanism is the release of the breaking agent through the rupture of the enclosure or encapsulating coating. Obviously, the bigger the capsules, the higher their probability of being crushed during the fracture closure. On the other hand, the encapsulated breaker has to be pumped downhole and therefore, as a rule, the size of the capsules of breakers is chosen similar to the size of the proppant.

[0013] The most commonly used proppant is made of sand grains having a size ranging between about 0.1mm and about 2mm, and most commonly between 0.2mm

and 0.5mm. Therefore, when a new material is studied to determine its suitability as an encapsulated breaker, a crucial limitation is its availability as granules with sufficient strength to survive the encapsulation process. Many solid materials are actually only available in powder form, passing through a sieve having an opening corresponding to 250 mesh according to the ASTM standard, or in other words, consisting of particles mostly ranging between 0.03mm and 0.05mm.

[0014] It should be further emphasized that even if the principal mechanism of release of breaking agent that is contemplated is not through crushing due to fracture closure but for instance, through dissolution or leakage of the enclosure. Coating a powder-like material usually result in some particles not or incompletely coated, at best using affordable technologies. Therefore, the breaking agent prematurely reacts with the crosslinked polymers so that the fluid may lose its suspending properties well before the proppant is properly placed in the fracture. For an effective encapsulation almost all particles have to be coated to prevent failure of the whole fracturing operation.

[0015] In the context of other fluid used in well services operations, such as cementing fluids, delayed release of some additives such as accelerators is also suitable. Though the particle size is not as critical as for fracturing fluids, it would be advantageous to be able to deliver some additives in encapsulated form.

[0016] The need for improved well services fluids still exists, and the need is met at least in part by the following invention.

#### **SUMMARY OF THE INVENTION**

[0017] It has been found that a large variety of solid chemicals available in a bulk powder form could be added to subterranean treatment fluids with delayed release when said chemicals are delivered as capsules consisting of encapsulated granulates obtained by aggregating the bulk powder under pressure to form a densified material and optionally, dry comminuting said densified material to produce granulates at the desired size.

[0018] Depending on the desired size, the densified material is obtained by roll compacting the bulk powder in a dry process to form a compacted sheet, then dry comminuted into granulates. As long as the extruded densified materials are larger than or equal to the desired particle size, it is not necessary to have a sheet prior to

granulation, so that for instance, briquettes larger than 20 mesh can first be prepared and then reduced to a size of 20/40 mesh suitable for most well stimulating applications.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0019] Figure 1 is a microscopic view (scale X60) of a powder (A), agglomerated with a binding material (B) and coated (C)

[0020] Figure 2 is a microscopic view (scale X60) of a powder (A), compacted into a sheet (D), granulated (E) and coated (F) according to the present invention

[0021] Figure 3 plots the percent of breaker released vs. time in minute with encapsulated agglomerates (open circles) and encapsulated granulates (full square).

#### **DETAILED DESCRIPTION OF THE INVENTION**

[0022] An inorganic sulfonate that is only available in powder form (having an average particle size of about 250 mesh) is shown in A. It can be agglomerated with binding material to produce particles in the size range of 20/40 mesh (B). However, the shape of the agglomerates is too irregular for encapsulation and the particles are also too weak to undergo the coating process. Part of the agglomerates will survive the coating process (Figure C). However, the release rate is very fast even with high coating level (Figure 3, solid squares).

[0023] In the context of well stimulation, the coating material preferably releases the encapsulated granulates to the well treatment fluid essentially by the crushing of the capsules due to the closure of the formation. In other cases, said enclosure is degraded under the conditions of pressure and temperature existing in the subterranean formation. Of course, a combination of the two release mechanisms, and others such as osmosis, may also occur and be favored depending on the applications.

[0024] The same material (A) can be processed into a densified sheet (D), which is then granulated into 10/40 mesh (E). These resulting particles are strong and can be encapsulated successfully at reasonable coating level (F). As shown in figure 3, open circles, in absence of a closure pressure, the core material release rate is almost nil.

[0025] The densified sheet is prepared by dry roll-compaction. In this process, the powder is typically pre-processed for precompaction and deaeration. Then the powder

is fed to the nip of compaction rolls capable of applying a compaction force of several metric tons to form a sheet-like structure having a thickness of about 2mm. The sheet may be broken into smaller sheets that are fed to crushing rolls that break them into granules. The powder is preferably precompacted and dearated before being delivered, for instance through a screw feeder into the roll nip area and seal system.

[0026] This dry process, known for years in the manufacture of fertilizers and pharmaceutical products, allows the fabrication of extremely dense granules that can easily receive a relatively uniform coating. Consequently, high coating levels are not required and the coating thickness may be adjusted as a function of the expected release time.

[0027] In some cases, a binder may be used to make the powder particles more "sticky".

[0028] The dry-roll compaction process allows the use of numerous chemicals that are chemically suitable as additive for oilfield services but only available as bulk powder. As a result, it is now possible to achieve controlled release of a much wider selection of chemicals.

[0029] Examples of such material include gel breakers such as polyelectrolytes (cationic or anionic), ionomers, nonionic polymers, and oxidizers. Other applications include well cementing additives such retarders, dispersing agents, fluid-loss control additives, set-accelerators, or extenders.

[0030] Examples of gel breakers are listed in the following table 1:

Polyelectrolytes	Cationic	Poly(2-vinylimidazolinium salt) Poly(N-vinylimidazolium salt) Poly(1-vinyl-2-methyl-2-imidazolium salt) Poly(N-vinylpiperidine)
	Anionic	Poly(acrylic acid) and its salts Poly(methacrylic acid) and its salts Poly(itaconic acid) and its salts Poly(crotonic acid) and its salts Poly(3-acrylamido-3-methylbutanoic acid) and its salts Poly(3-methacrylamido-3-methylbutanoic acid) and its salts Poly(naphthalene sulfonic acid) and its salts Poly(styrene sulfonic acid) and its salts Poly(ligno sulfonic acid) and its salts
Ionomers		Poly(4-vinylpyridine) Poly(ethylene-co-methacrylic acid) and its salts Poly(ethyl acrylate-co-4-vinylpyridine)

		Poly(ethyl acrylate-co-N-methyl-4-vinylpyridinium iodide) Poly(ethylene terephthalate-co-zinc sulfonate) Poly(styrene-co-methacrylic acid) and its salts Poly(styrene-co-styrenesulfonate) Polyamide-6 Poly(ethyl acrylate)
<b>Nonionic polymers</b>		Poly(ethyleneoxide) Poly(propylene oxide)
<b>Oxidizers</b>		Sodium peroxide Barium peroxide Hydrogen peroxide urea adduct Magnesium peroxide Potassium chlorate Potassium chromate Potassium dichromate Potassium iodate Nitrate Potassium nitrite Sodium perborate Oxides such as : <i>Chromium oxides, Magnesium oxides, Manganese oxides, Molybdenum oxides, Ferric oxides, Cobalt oxides, Tungsten oxides, Osmium oxides, Rhodium oxides, Iridium oxides, Ruthenium oxides, Nickel oxides, Zinc oxides, Zirconium oxides, Titanium oxides, Boron oxides, Beryllium oxides, Calcium oxides, Barium oxides, and Aluminum oxides</i>

**Table 1**

[0031] Among the materials listed above, salts of polynaphthalene sulfonic acid, having a molecular weight of about 7000 and salts of poly(styrene sulfonic acid) having a molecular of about 70,000 are more particularly preferred to be used as a breaker for zwitterionic surfactants such as betaine surfactants.

[0032] With well cementing, the delayed release of additives can result in improved control of cement slurry performance. For example, the performance of cement retarders can be improved by delaying their release until the cement has undergone the initial hydration period. Delayed release of accelerators can lead to improved control of the set time. Similar improvements in efficiency can be realized by delaying the release of fluid-loss additives, dispersants, etc. The particle size of the encapsulated granules is not as important for cementing as it is for encapsulated breakers for fracturing fluids. A wide range of particle sizes may be appropriate. Examples of additives suitable, for instance, in well cementing are listed in the following table 2:

Retarders/Dispersants	Sodium lignosulfonate
Fluid-Loss Control Additives	hydroxyethylcellulose hydroxypropylcellulose xanthans AA/AMPS copolymers carboxymethylhydroxyethylcellulose sulfonated polystyrene sulfonated copolymer of styrene/maleic anhydride sulfonated polyvinyltoluene
Accelerators	Aluminum sulfate Formate salts Aluminum chloride Iron sulfate
Extenders	Bentonite Superabsorbent polymers Attapulgite

**Table 2**

[0033] For a delayed release of the additive, the enclosure member is a key element. This enclosure is suitably any coating applied by a process that provides a substantially uniform coat or encapsulate individual particulate materials between 100 mesh to 5 mesh. By varying the coating thickness, the release characteristics can be varied to a large extent. A shorter release time will be obtained by thinner coating.

[0034] Two main types of coating process, top spray and bottom spray, are characterized by the location of the spray nozzle at the bottom or the top of a fluidized bed of solid particles. The nozzle sprays atomized flow of coating solution while the particles are suspended in the fluidizing air stream that carries the particles past the spray nozzle. The particles then collide with the atomized coating material as they are carried away from the nozzle in a cyclic flow. The temperature of the fluidizing air is set to evaporate solution or suspension liquid media or solidify the coating material shortly after colliding with the particles. The solidified coating materials will cover the particles gradually. This process is continued until each particle is coated uniformly to the desired coating thickness.

1. The properties of the coated particles can be tuned with the coating formulation, processing conditions, and layering with different coating material. The choice

of material will depend on a variety of factors such as the physical and chemical properties of the material being employed. Coating material can be from one of these categories: aqueous and organic solutions, dispersions, and hot melts. Non-limiting examples include acrylics, halocarbon, polyvinyl alcohol, Aquacoat® aqueous dispersions, hydrocarbon resins, polyvinyl chloride, Aquateric® enteric coatings, HPC, polyvinylacetate phthalate, HPMC, polyvinylidene chloride, HPMCP, proteins, Kynar®, fluoroplastics, rubber (natural or synthetic), caseinates, maltodextrins, shellac, chlorinated rubber, silicone, Coateric® coatings, microcrystalline wax, starches, coating butters, milk solids, stearines, Daran® latex, molasses, sucrose, dextrins, nylon, surfactants, Opadry® coating systems, Surelease® coating systems, enterics, Paraffin wax, Teflon® fluorocarbons, Eudragits® polymethacrylates, phenolics, waxes, ethoxylated vinyl alcohol, vinyl alcohol copolymer, polylactides, zein, fats, polyamino acids, fatty acids, polyethylene gelatin, polyethylene glycol, glycerides, polyvinyl acetate, vegetable gums and polyvinyl pyrrolidone.

What is claimed is:

1. A method for treating a subterranean formation which comprises injecting into the subterranean formation a well treatment fluid comprising a solid additive available in a bulk powder form, wherein said solid additive is delivered as capsules consisting of granulates encapsulated into an enclosure for a delayed release of said additive, said granulates obtained by a process including aggregating the bulk powder under pressure to form a densified material.
2. The method of claim 1, wherein the densified material is obtained by roll compacting the bulk powder in a dry process to form a compacted sheet.
3. The method according to any preceding claims, wherein the treatment is a hydraulic fracturing and granulates are in the size range of 20/40 mesh.
4. The method according to any preceding claims, wherein said enclosure comprises a coating material so that the solid additive is released to the well treatment fluid by the crushing of the capsules due to the closure of the formation.
5. The method of according to any preceding claims, wherein said enclosure is at least partially degraded under the conditions of pressure and temperature existing in the subterranean formation.
6. The method according to any preceding claims, wherein said solid additive is a gel breaker selected from the list consisting of polyelectrolytes (cationic or anionic), ionomers, non-ionic polymers, and oxidizers.
7. The method of claim 6, wherein said additive is a cationic polyelectrolytes selected form the list consisting of poly(2-vinylimidazolinium salt), poly(N-vinylimidazolium salt), poly(1-vinyl-2-methyl-2-imidazolium salt) and poly(N-vinylpiperidine).
8. The method of claim 6, wherein said additive is an anionic polyelectrolytes selected form the list consisting of poly(acrylic acid) and its salts, poly(methacrylic acid) and its salts, poly(itaconic acid) and its salts, poly(crotonic acid) and its salts, poly(3-acrylamido-3-methylbutanoic acid) and its salts, poly(3-methacrylamido-3-methylbutanoic acid) and its salts,

polynaphthalene sulfonic acid) and its salts, poly(lingo sulfonic acid) and its salts and poly(styrene sulfonic acid) and its salts

9. The method of claim 6, wherein said additive is an ionomer selected from the list consisting of poly(4-vinylpyridine), poly(ethylene-co-methacrylic acid) and its salts, poly(ethyl acrylate-co-4-vinylpyridine), poly(ethyl acrylate-co-N-methyl-4-vinylpyridinium iodide), poly(ethylene terephthalate-co-zinc sulfonate)), poly(styrene-co-methacrylic acid) and its salts, poly(styrene-co-styrenesulfonate), polyamide-6, and poly(ethyl acrylate).
10. The method of claim 6, wherein said additive is a nonionic polymer selected from the list consisting of poly(ethyleneoxide) and polypropylene oxide.
11. The method of claim 6, wherein said additive is an oxidizer selected form the list consisting of sodium peroxide, barium peroxide, hydrogen peroxide urea adduct, magnesium peroxide, potassium chlorate, potassium chromate, potassium dichromate, potassium iodate, potassium nitrate, potassium nitrite, sodium perborate and poly(propylene oxide).
12. The method according to any preceding claims, wherein said solid additive is a well cementing additive selected from the list consisting of dispersing agents, fluid-loss control additives, set-accelerators, and extenders.
13. The method of claim 12, wherein said solid additive is a dispersing agent selected from the list consisting of sodium lignosulfonate, calcium lignosulfonate, poly(naphthalene sulfonate), poly(melamine sulfonate), and amine phosphonates.
14. The method of claim 12, wherein said solid additive is a fluid loss control additive selected from the list consisting of hydroxyethylcellulose, hydroxypropylcellulose, xanthans, AA/AMPS copolymers, carboxymethylhydroxyethylcellulose, sulfonated polystyrene, sulfonated copolymer of styrene/maleic anhydride, and sulfonated polyvinyltoluene.
15. The method of claim 12, wherein said solid additive is an accelerator selected from the list consisting of aluminum sulfate, formate salts, and aluminum chloride.

16. The method of claim 12, wherein said solid additive is an extender selected from the list consisting of bentonite, superabsorbent polymers, and attapulgite.

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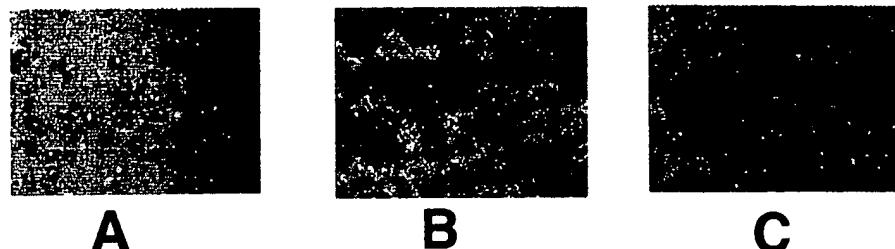
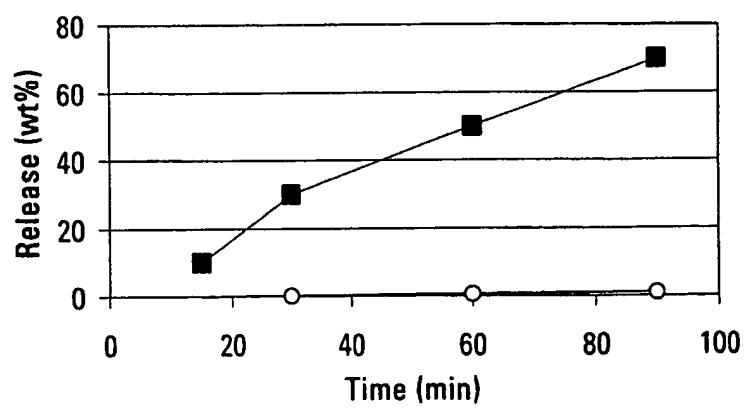


FIG. 1



FIG. 2

FIG. 3



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/06188

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 E21B43/26 E21B43/25

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 741 401 A (WILLIAMSON TREVOR D ET AL) 3 May 1988 (1988-05-03) cited in the application column 2, line 44 - column 3, line 18 column 4, line 3 - line 32 column 5, line 18 - line 32 column 6, line 13 - column 7, line 7 column 7, line 53 - column 8, line 12 -----	1-6,11
Y	EP 0 275 624 A (PETROLITE CORP) 27 July 1988 (1988-07-27) column 5, line 43 - column 6, line 16 column 8, line 6 - line 38 -----	1,3,5,6, 11
Y,P A,P	US 2002/193257 A1 (LEE JESSE C ET AL) 19 December 2002 (2002-12-19) paragraph '0012! - paragraph '0027!; claims 1,2,9-17 -----	1,4,6 7,8
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

16 October 2003

Date of mailing of the international search report

27/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Boulon, A.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/06188

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 958 638 A (JOHNSTON CHESTER C) 25 May 1976 (1976-05-25) column 3, line 13 - line 35 column 5, line 53 - column 6, line 18 -----	1,2,5, 12,15
Y	US 4 036 401 A (NACHTIGALL JR WALTER E) 19 July 1977 (1977-07-19) column 4, line 26 - line 40 -----	1,12,15

## INTERNATIONAL SEARCH REPORT

International Application No
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